DEVELOPMENT OF BRISTOL GLAZE BY USE OF PHOSPHATES

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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THE DEVELOPMENT OF BRISTOL GLAZE BY USE OF PHOSPHATES.

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INTRODUCTION.

The term Bristol glaze seems to have come from the town in England called Bristol. From all reports this seems to be the origin of the name of what is now called the Bristol glaze of today. This type of glazes is well adapted for use on stoneware, terra cotta, brick, and porcelain bodies. Up to 1885, all stoneware seems to have been glazed with sodium chloride and Albany slip. The use of a lead glaze for such ware was limited and due to the effects of the lead on the glaze workers the lead content in the various stoneware glazes was eliminated gradually and substituted with zinc oxide. At last, all lead was removed and a white opaque glaze resulted. In 1884 the Bristol glaze was exhibited at New Orleans, and from all reports this was the first appearance of the Bristol glaze in this country. Some authorities differ as to whether the glaze was first used in America or England. However, about 1884 seems to mark the beginning of the use of such a glaze in this country. The earlier forms were applied by rolling the ware in clay and flint. The ware was burned and the customary salt glaze applied. This method gave a glaze very much like the present day Bristol, both in appearance and composition. (1).

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From notes on lecture on "Glazes" by Prof. C. W. Parmelee, University of Illinois. (1).

Since the year of 1884, the Bristol glaze has developed until now it plays an important part in the stoneware industry. Variations have been made, but, in the main, the glaze is composed of three fluxes: potassium oxide, calcium oxide, and zinc oxide; the intermadiate, alumina; and the acid constituent, flint. (1).

Up to the present date, there has been little or no work done on the effect of phosphates on a Bristol glaze. There have been several ideas carried out regarding the addition of small portions of bone ash, and one investigation by Prof. C. W. Parmelee on the effects of aluminum phosphate on glaze behavior. (2). It was due to the suggestion of Prof. C. W. Parmelee, that this investigation was undertaken, and the author wishes to thank him for the aid and support rendered during the experimenting.

It was the purpose of this investigation to see what effect various phosphates had on the development of a Bristol glaze; to study carefully their behavior and at the same time find out what would be the best glaze compositions.

The glaze develops and matures around cone 5 and cone 8, is generally used on stoneware and terra cotta, and in some instances, brick and porcelain bodies. Due to the nature of the glaze, it can be used on ware either bone dry or leather, and can be burned in unwadded saggers.

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(1). Notes on lecture on "Glazes" by Prof. C. W. Parmelee.
(2). Transactions American Ceramic Society, Volume 8, Page 237.

II. PROCEDURE AND SURVEY OF WORK.

The type formula used was one which develops at about cone 6, (1250° C.),in from 36 to 40 hours. The ceramic formula for this glaze is as follows;

$$\left.\begin{matrix} .333 & K_2O \\ .333 & CaO \\ ,333 & ZnO \end{matrix}\right\} \quad .55 \quad Al_2O_3 \quad \left\{ \quad 3.3 \quad SiO_2. \right.$$

Three phosphates: aluminum, calcium, and barium, were used as the main variables, with zinc phosphate used occasionally to fill in and give the required P_2O_5 content. This investigation consisted mainly of three series, namely: Series I, made up by the use of aluminum phosphate giving as variables P_2O_5 and Al_2O_3; Series II, made up by the use of calcium phosphate, giving as variables P_2O_5, CaO,and ZnO, the latter varying together; and Series III, made up by the use of barium phosphate, giving as variables P_2O_5, and BaO, and ZnO, the latter varying together.

The materials used were:

Potassium Carbonate (K_2CO_3)	source giving	K_2O.
Calcium Carbonate ($CaCO_3$)	source giving	CaO
Calcium Phosphate $Ca_3(PO_4)_2$	source giving	CaO and P_2O_5
Zinc Oxide (ZnO)	source giving	ZnO
Zinc Phosphate $Zn_3(PO_4)_2$	source giving	ZnO and P_2O_5
H. & G. A-1 English China Clay	giving	$Al_2O_3$and SiO_2
Flint	giving	SiO_2
Barium Carbonate ($BaCO_3$)	source giving	BaO
Barium Phosphate $Ba_3(PO_4)_2$	source giving	BaO and P_2O_5

The batches were mixed and ground wet from 4 to 5 hours in glaze pebble mills. They were then lawned through 120 mesh and the specific gravity adjusted to about 24 ounces to the pint.

The variable glaze compositions were made up by blending the extremes to get the intermediates. The blending was done by weight on the batch weight basis. The glazes were then dipped on Bloomingdale stoneware trial pieces, and prepared for burning.

The trial pieces were made up of the above mentioned clay prepared by pugging in a wet pan and running the plastic clay through an auger machine. The trial pieces were cut and dried in a steam dryer until they were "bone dry".

The firing was done in coal-fired, down-draft test kilns, burning bituminous coal of a fairly good grade. The ware was set in unwadded saggers, and burned at three cones: namely, 3, 6, and 10, and burned for 40 hours.

III. CERAMIC FORMULAS AND WEIGHTS.

In order to use phosphates only to give the P_2O_5 content there are certain limits within which the formulas had to stay. The ceramic formulas with the variables for each series are as follows:

Series I.

$$\left.\begin{matrix} .333 & K_2O \\ .333 & CaO \\ .333 & ZnO \end{matrix}\right\} \quad .3 - .6 \quad Al_2O_3 \quad \left\{\begin{matrix} 3.3 & SiO_2 \\ .05\text{-}.3 & P_2O_5 \end{matrix}\right.$$

Series II.

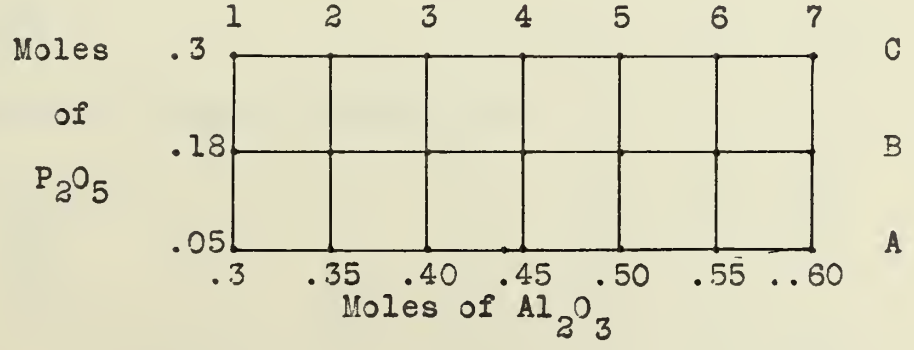
$$\left.\begin{matrix} .300 & K_2O \\ .14\text{-}.42 & CaO \\ .56\text{-}.28 & ZnO \end{matrix}\right\} \quad .55 \quad Al_2O_3 \quad \left\{\begin{matrix} 3.3 & SiO_2 \\ .07\text{-}.21 & P_2O_5 \end{matrix}\right.$$

Series III.

$$\left.\begin{matrix} .300 & K_2O \\ .0 - .4 & BaO \\ .4 - .0 & CaO \end{matrix}\right\} \quad .55 \; Al_2O_3 \quad \left\{\begin{matrix} 3.3 & SiO_2 \\ .1\text{-}.2 & P_2O_5 \end{matrix}\right.$$

Series I.

Diagram of Field of Series I.

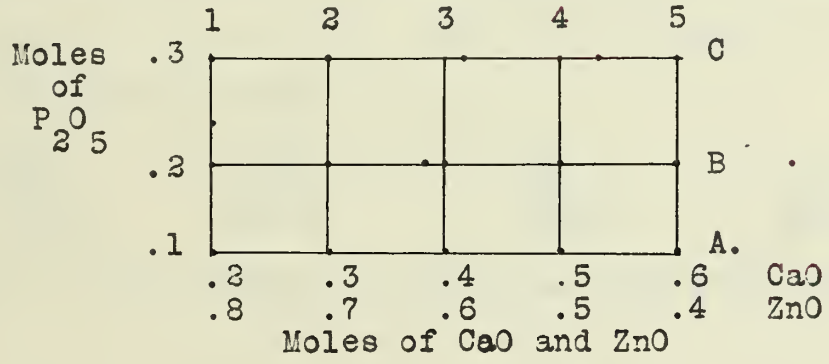


The batch weights of the extremes of the first series are given as follows:

A-1.		A-6.		C-1.		C-6.	
K_2CO_3	46.0	K_2CO_3	46.0	K_2CO_3	46.0	K_2CO_3	46.0
$CaCO_3$	33.3	$CaCO_3$	33.3	$CaCO_3$	33.3	$CaCO_3$	33.3
ZnO	27.0	ZnO	27.0	ZnO	27.0	ZnO	27.0
$AlPO_4$	12.2	$AlPO_4$	12.2	$AlPO_4$	73.2	$AlPO_4$	73.2
Clay	64.5	Clay	142.0	Clay	----	Clay	77.4
Flint	168.0	Flint	132.0	Flint	198.0	Flint	102.0

Series II.

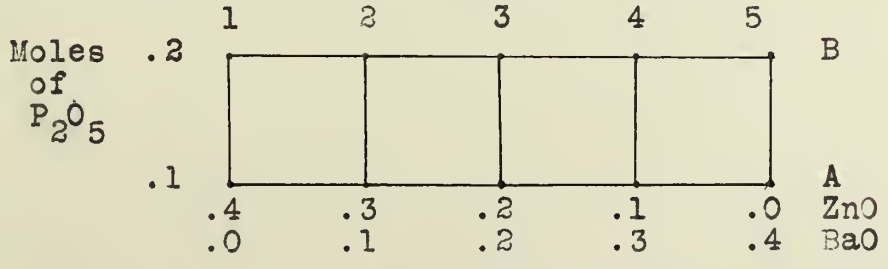
Diagram of Field Of Series II.



A-1.		A-5.		C-1.		C-5.	
K_2CO	59.5	K_2CO_3	59.5	K_2CO_3	59.5	K_2CO_3	59.5
ZnO	26.5	ZnO	32.4	ZnO	8.1	ZnO	8.1
$Ca_3(PO_4)_2$	18.3	$Ca_3(PO_4)_2$	27.8	$Ca_3(PO_4)_2$	18.3	$Ca_3(PO_4)_2$	55.6
$Zn_3(PO_4)_2$	13.1	$CaCO_3$	30.0	$Zn_3(PO_4)_2$	89.5	$Zn_3(PO_4)_2$	38.5
Clay	202.5	Clay	202.5	Clay	202.5	Clay	202.5
Flint	188.0	Flint	188.0	Flint	188.0	Flint	188.0

Series III.

Diagram of Field of Series III.



A-1.		A-5.		B-1.		B-5.	
K_2CO_3	41.4	K_2CO_3	41.4	K_2CO_3	41.4	K_2CO_3	41.4
ZnO	24.3	ZnO	24.3	$Zn_3(PO_4)_2$	38.5	$Zn_3(PO_4)_2$	38.5
$Ca_3(PO_4)_2$	31.0	$Ba_3(PO_4)_2$	60.1	$Ca_3(PO_4)_2$	31.0	$Ba_3(PO_4)_2$	60.1
$CaCO_3$	10.0	$BaCO_3$	19.7	$CaCO_3$	10.0	$BaCO_3$	19.7
Clay	142.0	Clay	142.0	Flint	132.0	Flint	142.0
Flint	132.0	Flint	132.0	Clay	142.0	Clay	142.0

In calculating the glaze compositions and blending to get the intermediates, the batch weight method was used. As an example, say there are four glazes, each varying in composition as in the above glazes. The intermediates are obtained by, first mixing up the extremes, and then dividing the extremes up into parts as follows;

A.	B.	C.	D
100% A.	66% A.	33% A.	0% A.
0% D.	34% D.	66% D.	100% D.

The 100% of A for instance is taken as 100% of the batch weight.

IV. SERIES I.- ALUMINUM PHOSPHATE.

The formula and method of procedure was given above, hence this division and the two divisions following give the results obtained in both dipping and burning the glazes.

The oxygen ratio of these glazes range from 2.9 - 4.0. The Al_2O_3-SiO_2 ratio range from 1/5.5 to 1/6.

The glaze extremes were weighed and found to be as follows:

A-1..... 23.2 ounces per pint.
A-6..... 24.6 ounces per pint.
C-1..... 24.2 ounces per pint.
C-6..... 25.6 ounces per pint.

When these glazes were blended as described above the specific gravity ranged from 23.2 to 25.5. This was about the correct consistency for dipping.

As a whole, the glazes dipped well, except in a few cases and then spraying was resorted to which proved a remedy.

Results of Cone 3: This cone temperature was not sufficiently high. The glazes in general were immature and appeared to be merely sintered. There are a few results that were very obvious that may be well to mention. With a low Al_2O_3 content glazes were immature. With increasing P_2O_5 the fusibility seemed to increase. The color was about the same throughout the variations, the only color being a white with a gradual darkening as P_2O_5 and Al_2O_3 increase. As a whole the glazes were poorly developed giving none that was good.

Results of cone 6: The results of this temperature were very similar to the cone 3 burn. The increase in heat treatment showed little change in the maturity of the glazes. With an increase in P_2O_5 content the fusibility increased which leads to the conclusion that this is true in general. There was no apparent effect upon the color, because the RO group content remained constant, and upon this group depends the constituents for giving the color. The results of this temperature show no signs of any glaze possibilities at this cone.

Results of cone 10: The results of this burn were a little more satisfactory than the lower cones. The trial pieces did not withstand this temperature and were consequently overburned. This only made it a little more difficult to judge the glazes. The glazes of low Al_2O_3 content showed no signs of maturity as in the above cases, but as the Al_2O_3 content increased an increasing maturity resulted until the glazes were of a glossy texture. Glazes A-4, B-4, C-4, A-5, and above were the best ones. Of these, glaze A-4 proved the best. At this temperature the glazes appeared transparent with the gray color of the body imparted to the glaze. In general, this series required about cone 10 the develop the glaze.

V. SERIES II. - CALCIUM PHOSPHATE.

The oxygen ratio of this series range from 2.6 to 2,9. The Al_2O_3-SiO_2 ratio was constant at 1/6.

The glazes of this series dipped with better results than Series II. In fact the dipping properties were good. The specific gravity of these glazes was about 25 ounces per pint.

Results of cone 3: The glazes of this series were not matured as in Series I and cone 3 burn. The same results were apparent regarding the increasing P_2O_5 content. The glazes at this temperature crawled a little.. This, perhaps, was due to the high raw clay content. To remedy this the raw clay should be calcined and should not be added much above .3 equivalents. The color of these glazes was white. This was due to the zinc oxide content in the glaze. In general there were no glazes that turned out well.

Results of cone 6: There were no good glazes developed, but the glazes showed more signs of maturity.

Results of cone 10: The results of this burn were the best in comparison to the other cone temperatures. The decreasing ZnO and increasing CaO glazes became more transparent which may be due entirely to the decrease in ZnO content. The increased fusibility due to increased P_2O_5 content was again evident. All glazes except A-1, A-2, A-3, and A-4 were good. They developed a good glossy texture, but were transparent giving the grayish color of the body. The glazes showed no signs

of crazing or crawling. The gloss developed at this temperature was good, and especially this was true with glaze A-4.

V. SERIES III. - BARIUM PHOSPHATE.

The oxygen ratio lies within the range of 2.7 to 2.9, while the Al_2O_3-SiO_2 ratio remained the same value of 1/6.

The specific gravity for this series was made to be about 24.0 to 25.0 ounces per pint. This series resembled Series II in dipping properties. The trial pieces dipped well giving a good smooth finish.

Results of cone 3: This series developed the best glazes of all three series. Glazes B-3, B-4, and B-4 were matured with a fair glossy texture. Of all these, glaze B-4 was the best. This glaze is, perhaps, the only satisfactory one at this cone while at a higher cone much better glazes developed. The color of these glazes was a grayish white.

Results of cone 6: As might be expected the increased heat treatment given the poor glazes greatly improved the nature of the glazes above those of cone 3. Still the glazes of low P_2O_5 content showed signs of immaturity, but glazes B-1, B-2, B-3, B-4, and B-5 were all developed with a good glossy texture. Of all these glazes B-3 was the best. The others showed signs of crawling slightly. Glaze B-3 gave a good gloss, and was gray in color. The amount of crawling mentioned above can be remedied easily and will give several good glazes.

Results of cone 10: The results of this burn were good. Glazes were matured giving a fair glossy texture. There was no crazing, crawling, and the glaze was transparent with the gray of

the body showing through. All the glazes developed alike showing little variation. This burn resulted in some good glazes, but the best were the ones of about a one to one ratio of CaO and ZnO.

VII. DISCUSSION OF RESULTS.

A comparison of the oxygen and alumina-silica ratio is desirable. As given by several authorities, the oxygen ratio for a Bristol glaze should be from 2.3 to 2.5. The alumina-silica ratio is usually around 1/6 to 1/7. The glazes falling under these classifications are supposed to mature satisfactorily. It is possible, however, to lower the alumina-silica ratio with a low alumina content and run into the field of good matt glazes.

Under Series I, the oxygen ratio ranges from 2.9 to 6.0. According to the results it was very evident that glazes with oxygen ratio above 2.7 were not developed. One might conclude, then, that the composition was impossible as a glaze and would not develop under any consideration. The alumina-silica ratio given for a Bristol glazeis usually 1/6 to 1/7. This comparison shows that ratio given above for these glazes is about normal.

Under Series II. the oxygen ratio was 2.6 to 2.9 and the alumina-silica ratio was 1/6. Both of these ratios prove satisfactory according to the requirements and in comparison with the results, this is true because the glazes developed far better in this series than in Series I.

The ratios for Series III are 2.7 to 2.9 for the oxygen ratio and 1/6 for the alumina-silica ratio. The same is true of Series III as is true of Series II in regard to the correct ratios for the glazes compositions. However, Series III glazes developed much better than Series I. In general that best glazes fell with-

in the limits of the oxygen and alumina-silica ratios of typical Bristol glazes.

It might be well to discuss the body used in this investigation. The Bloomingdale stoneware body used worked nicely at cone 3 and cone 6, but when cone 10 was reached the body showed signs of overburning. It is possible to develop these glazes on porous tile trial pieces, which would prove better at the higher temperature. Due to this overburning, it was rather hard to judge the glazes to any advantage at cone 10.

There was a great deal of flaking and cracking of some of the glazes. This was not true of all, but those glazes that were bad were not improved when sprayed. The author is of the opinion that a substitution of ball clay and calcined kaolin for some of the raw clay would give the glazes better dipping properties. From all indications the dipping properties had little effect in the development of the phosphate Bristol glazes, but such remedies would prove beneficial for some of the glazes.

A fusion test was run on the extremes of the various series and not much could be learned from the results. The glazes were made up in cones and placed along side of standard cones. The results showed that the glazes went down at cone 3 to cone 4.

VIII. CONCLUSIONS.

In concluding there are several general results which may be stated. These follow time after time and are facts proven. They will be given at the end of this section. There are several difficulties arising when developing a Bristol glaze by the use of phosphates. This investigation does not complete the work that is at all possible, but it reveals several difficulties that should be overcome should such an investigation be tried further. The author is of the opinion that by reducing the alumina-silica content, still keeping the proper ratio, i. e., 1/6 to 1/7, the flux content would be increased in proportion and this would make a less refractory glaze. What is desired is a glaze which develops at about cone 6. The Bloomingdale stoneware will not stand a higher temperature with good results. It is also suggested that biscuit trial pieces be used. This will allow a higher temperature to be used to develop the glazes.

In Series II there appeared a solution of the ZnO with increasing P_2O_5 content giving transparency.

Through all series an increase in P_2O_5 content caused fusibility to increase.

ZnO and BaO developed better glazes than ZnO and CaO and were best at equal parts of ZnO and BaO.

With an increase in P_2O_5 content the ZnO was taken up in solution more, resulting in a more transparent glaze.

XI. BIBLIOGRAPHY.

There is not much literature on this subject, but what was at all available, the author went over and picked out the most important parts.

In Chemical Abstracts, 1909, 5:3685, K. Huthrer says, "When extremely finely pulverized SiO_2 is heated with an excess of H_3PO_4 in a quartz tube, a clear solution results, first. On further heating, a white pulverent precipitate separates which appears under the microscope as a mixture of fine rods, hexagonal plates and octahedra. Analysis shows that it has the composition $SiO_2.P_2O_5$, and the name Silicyl Phosphate has been chosen. The compound may be prepared also by heating for a long time in a platinum dish, a mixture of $SiCl_4$ and H_3PO_4. At ordinary temperatures it is fairly stable and decomposes only before the oxy-hydrogen flame. At moderate temperatures P_2O_5 is slowly driven off and the crystalline form disappears. Heated in a current of steam a steady loss in weight occurs. It resists the attack of strong acids except HF, but is decomposed by NaOH and Na_2CO_3. Just as SiO_2 is attack by H_3PO_4, so also is glass. The results of a number of experiments may be summed up in the statement that in the latter case the following compounds may be produced: SiP_2O_7, $NaPO_3$ or KPO_3, $Ca_3(PO_4)_2$ and $AlPO_3$."

In Chemical Abstracts, Volume 10, 2036, C. H. Kerr says: "Bone ash should be used with KNO_3 and As_2O_3 to increase fluidity. Adding a small amount of Pb_3O_4 makes a softer and more brilliant

glass, especially good for taking colors. Some borax should also be used".

In Chemical Abstracts, volume 11, 2709, C. G. Memminger says: "Natural phosphates containing SiO_2 and $CaCO_3$ are calcined at 1400-1500° C. to drive off volatile matter and decompose the $CaCO_3$, yielding CaO which combines with SiO_2. The $Ca_3(PO_4)_2$ is not affected."

In Chemical Abstracts, volume 13, 1002, H. Fritz says: "Glasses and glazes were prepared from mixtures of PbO, alkalies, lime, BaO, or ZnO, and P_2O_5 or a phosphate. When a phosphate was used the products were not clear, but when P_2O_5 was used, they were mostly clear and occasionally brilliant. In some cases the introduction of .15 equivalents of Al_2O_3 made a turbid glass or glaze become more clear. Most of the glazes prepared with P_2O_5 were subject to crazing. Brilliant glazes free from crazing were obtained, however, with a mixture of the compounds. (0.1 K_2O, 0.1 CaO, 0.8 PbO, 0.3 Al_2O_3, and 2.0 P_2O_5. "

In the Transactions of the American Ceramic Society, volume 7, page 205, Binns says: "Calcium phosphate is practically infusible, and there is no doubt that its function in a body is to uphold the mixture and to enable it to endure a more severe fire than it otherwise would." The same volume on page 274, he states that the effect of bone ash in ceramic mixtures is highest in fusibility at 17%. The physical structure of the bone has no effect. The infusibile character of the bone china depends upon an excess of bone.

In Transactions of the American Ceramic Society, volume 10, page 241, Stull says: "The use of bone ash is a direct cause of flaking of the glaze. Flaking is overcome by calcining the bone ash with flint. Replacement of CaO from whiting by CaO from bone ash increases refractoriness materially and induces crazing." In volume 10 page 243, he also says: " Bone ash is used as an opacifier in glazes; excess of opacifier causes beading."

In the Transactions, volume 8, page 237: Prof. C. W. Parmelee says: "Presence of phosphoric acid gives translucency if in sufficient amounts and tends toward improvement in color; acts as a flux and vitrifying agent. With a slight increase of SiO_2, fusibility is increased. Presence of 0.2 equivalents of potash does not effect translucency, but increases fusibility and causes the enamel-like appearance." This was on a body composition.

X. ACKNOWLEDGMENT.

It was due to the aid and support of Prof. C. W. Parmelee, that this investigation was carried on and the author wishes to take this means of expressing thanks for such suggestions.